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PROCESSING STUDIES OF BITUMENS/HEAVY OILS PRODUCED BY RECOVERY METHODS OF A DIVERSE NATURE

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PROCESSING STUDIES OF BITUMENS/HEAVY OILS PRODUCED BY RECOVERY METHODS OF A DIVERSE NATURE

Final Report

by

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SUMMARY

The project objective was to develop a data base of the processing characteristics and product qualities of bitumens and heavy oils produced by a variety of recovery methods. The ease of processing a specific feedstock is relative to its source and method of recovery. Coking propensities, which variously influence the test catalyst performance and hence the process product yield patterns, are also affected by the recovery technique.

Five 343°C+ resid fractions, derived from Murphy Eyehill fireflood enhanced oil recovery (EOR) and primary production heavy oils, Cold Lake bitumen extracted from core, and Marguerite Lake bitumen produced by a combination of steam and fireflood EOR methods were used for the experiments. Both the desalted and undesalted versions of the Eyehill primary crude were evaluated. Feedstocks from the same or a similar bitumen/heavy oil production locale were evaluated under identical process unit operating parameters.

Hydroprocessing (catalytic hydrocracking/hydrotreating) experiments were performed to determine the degree of removal of contaminants (sulphur, nitrogen and trace metals), liquid product and gas yield distribution structure, conversion of resid (525°C+) fraction and to assess the response of each feedstock to typical hydrocracking conditions.

Reactor plugging played a major role in determining the duration of each feedstock experiment. Several experiments were terminated prematurely because of a reactor plugging problem. Two possible causes of the reactor plugging were identified; high salt content in the feed and reactor coking. Despite these problems each experiment, except that involving the Marguerite Lake feedstock, was of sufficient duration to provide the data that allowed a fairly complete assessment of the processing performance of the feedstock.

The experimental data indicate that of all the Murphy Eyehill heavy oil feedstocks tested, the EOR sample had the best conversions on the basis of the sulphur, nitrogen and 525°C+ resid conversions achieved. The catalyst's ability to maintain a constant desulphurization activity for an extended period was best with the desalted feedstock.

The Cold Lake bitumen resid processed easily when compared to the Marguerite Lake bitumen resid. Reactor coking terminated the Marguerite Lake experiment after only two days of operation.

It is the conclusion of the authors' project that the Murphy Eyehill heavy oil produced by a fireflood EOR technique had a superior hydroprocessing performance when compared to the primary crude counterpart. The contribution of the iron in the EOR sample is believed to be the main difference. The Cold Lake bitumen extracted from core was easily upgraded when compared with the Marguerite Lake sample. The Marguerite Lake bitumen data were limited, but indicated a significant coking tendency. The Eyehill results also show that salt removal is an important step in feedstock preparation.

SOMMAIRE

L'objectif du projet était d'élaborer une base de données des caractéristiques de traitement et des qualités des bitumes et huiles lourdes produits par une variété de méthodes d'extraction. La facilité avec laquelle on traite une charge d'alimentation donnée dépend de sa source et de sa méthode d'extraction. La tendance à la cokéfaction est également affectée par la méthode d'extraction; cette tendance à la cokéfaction affecte grandement le rendement des catalyseurs en présence desquels on procède aux tests et donc la production finale selon le procédé choisi.

Lors des expériences, nous avons utilisé cinq fractions résiduaires à 343°C+, dérivées de la méthode d'extraction améliorée par injection Murphy Hill (EOR) et des huiles lourdes de production primaire, du bitume de Cold Lake extrait d'une carotte-témoin, et du bitume de Marguerite Lake produit par une combinaison de méthodes comprenant la vapeur et l'injection EOR. Nous avons procédé à l'évaluation des pétroles bruts primaires de Eyehill dans les versions dessalée et non-dessalée. Nous avons évalué des charges d'alimentation provenant du même lieu de production ou d'un lieu de production semblable d'huile lourde et de bitume, selon des paramètres de fonctionnement identiques de l'unité de traitement.

Nous avons procédé à des expériences d'hydrotraitement (hydrocraquage/ hydrotraitement catalytique) pour déterminer le degré d'élimination des agents contaminants (composés sulfurés, azote et oligo-éléments), la structure de distribution de rendement en produits liquides et gazeux, la conversion de la fraction résiduaire à 525°C+. Nous voulions également évaluer la réaction de chaque charge d'alimentation aux conditions typiques d'hydrocraquage.

L'engorgement du réacteur a joué un rôle important pour déterminer la durée de l'expérience pour chaque charge d'alimentation. Plusieurs expériences ont dû être arrêtées prématurément du fait de problèmes d'engorgement du réacteur. Deux causes possibles en ont été identifiées: haute teneur en sel de la charge d'alimentation et cokéfaction au niveau du réacteur. Malgré ces problèmes, toutes les expériences, sauf celle faite sur la charge de Marguerite Lake, ont été d'une durée suffisante pour permettre de recueillir des données rendant possible une évaluation assez complète du rendement du traitement des charges d'alimentation testées.

Les données expérimentales indiquent que, de toutes les charges d'huile lourde de Murphy Eyehill testées, l'échantillon EOR offrait les meilleures conversions, en se basant sur la conversion des composés sulfurés, de l'azote et des résidus 525°C+ obtenue. La capacité du catalyseur à maintenir une activité constante de désulfurisation pendant une période prolongée s'est révélée meilleure avec la charge d'alimentation dessalée.

Le résidu bitumineux de Cold Lake a été traité facilement par rapport à celui de Marguerite Lake. Des problèmes d'engorgement du réacteur ont obligé l'expérience sur le bitume de Marguerite Lake à s'arrêter après seulement deux jours.

Les auteurs du projet concluent que l'huile lourde Murphy Eyehill produite par la technique d'injection EOR a présenté un rendement supérieur d'hydrotraitement par rapport aux autres pétroles lourds primaires testés. Nous sommes d'avis que c'est le fer dans l'échantillon EOR qui a contribué à faire la différence. Le bitume de Cold Lake extrait de la carotte-témoin a été traité facilement par rapport à l'échantillon de Marguerite Lake. Les données sur le bitume de Marguerite Lake étaient limitées, mais ont indiqué une tendance certaine à la cokéfaction. Les résultats se rapportant à l'échantillon de Eyehill montraient également l'importance de l'extraction du sel dans la préparation de la charge d'alimentation.

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1. INTRODUCTION

1.1 Background

The source and the method of recovery of bitumen and heavy oil can change their processing characteristics. Coking tendencies and product yield patterns can be affected. This is especially true if the recovery method subjects the oil to thermal conditions. Removal of the various contaminants, such as sulphur, nitrogen and trace metals, may be more difficult with the thermally-altered oil.

Canada's production of bitumen and heavy oil is increasing as conventional reserves are depleted. Synthetic crude production is also expanding as upgrading facilities are built or expanded. With a growing competitive crude market, identification and understanding of the relevant processing characteristics of these heavy oil resources are important in their efficient utilization.

The processing of bitumen and heavy oil produced by a variety of recovery methods was the principal focus of the project. The program evaluated five bitumen/heavy crude samples (produced using four different recovery techniques) from three different sources. These included primary and EOR (fireflood) feedstocks from the Murphy Eyehill oil fields, crude derived from bitumen extracted from core produced in the Cold Lake area, and Marguerite Lake bitumen crude produced by a combination of steam and fireflood EOR techniques. Separate Marguerite Lake samples, one produced by in-situ combustion and one by steam, were to be tested, but it was found that samples affected by only one EOR technique could not be obtained.

After completion of the experiments on the Murphy Eyehill EOR and the undesalted primary feedstocks, it was suspected that salt was causing some of the differences in the processing characteristics of the Eyehill primary feedstock. The experimental program was therefore expanded to include an additional test of a desalted Eyehill primary resid sample. The purpose was to determine the effect of the salt content of the feedstock.

The project objective was to develop a data base of bitumen and heavy oil feedstocks with respect to their processing characteristics and product qualities. The experimental program was designed and conducted so that the differences among the feedstocks would be readily assessable. The feedstocks were prepared, where required, in a similar manner and subjected to identical continuous fixed-bed hydroprocessing conditions.

The processing characteristics were measured by a number of factors. The degree of removal of the feed contaminants, such as nitrogen, sulphur and trace metals, was one measure. Yield distribution of naphtha, distillate, resid fraction and gas was a second measure. Assessment of catalyst deactivation rate, visual appearance of the catalyst after the completion of the testing and qualitative assessment of the general operability of the process unit were also considered in determining the processing behaviour of a specific feedstock.

II. EXPERIMENTAL

2.1 Feedstock History

The feedstocks evaluated were a variety of bitumen and heavy oil crudes. Whole crude samples of EOR (fireflood) and primary production crudes produced from the Murphy Eyehill project area were obtained. The desalted and undesalted forms of the primary crude were evaluated. A sample of crude from Cold Lake bitumen extracted from core was obtained from the Alberta Research Council (ARC). The Marguerite Lake feedstock, also obtained from ARC, was derived from bitumen produced by a combination of steam and fireflood EOR techniques.

The Eyehill feedstock analyses are provided in Tables 1, 3 and 5. The three Murphy Eyehill samples had similar properties with the exception that the EOR variety possessed the highest level of trace metal contaminants. Of particular note is the high level of iron (611 wppm) in the EOR sample relative to 48.2 and 49.8 wppm for the undesalted and desalted feedstocks, respectively.

The characteristics of the Cold Lake and Marguerite Lake feedstocks are also comparable. The Marguerite Lake resid, however, had higher levels of trace metals particularly nickel and vanadium and toluene insoluble material. The analyses of the Cold Lake and Marguerite Lake samples are provided in Tables 7 and 9.

2.2 Feedstock Preparation

The Cold Lake feedstock was prepared by distilling about 25 L of the whole crude sample using a short path distillation apparatus (wiped film evaporator). Two distillation steps were followed. The first step, performed at atmospheric pressure, removed water and fractions boiling below

210°C. The second step, conducted under vacuum, removed the fraction below 343°C to yield a 343°C+ resid used for the processing experiments. The undesalted Eyehill primary and EOR feedstocks were prepared in a similar manner.

The Marguerite Lake sample, which contained approximately 2 vol % water as received, was distilled to produce a 343°C+ resid fraction using ASTM method D-2592. This method uses a column with at least 15 theoretical separation stages. Approximately 7 L of resid was distilled from 20 L of sample.

The desalted form of the Eyehill primary crude was evaluated. The purpose was to assess the effect of the salt content on the processing characteristics of the feedstock. The whole crude sample was desalted by performing extractions with distilled water. Toluene was added to reduce the viscosity of the crude and expedite the desalting. A small amount of demulsifying chemical (to facilitate the removal of water) was added to the crude, which was then allowed to sit overnight under gentle heating. The water/toluene mixture was drained and the salt level determined.

Desalting the material twice was required to produce a cleaned, desalted feedstock having a salt content of 0.0408 kg/m³ (14.3 lbs/1000 barrels). The initial desalting reduced the salt content to 0.24 kg/m³ (71.5 lb/1000 barrels). Remnants of toluene and water in the sample were removed during initial atmospheric distillation performed with a short path distillation apparatus. The 343°C+ resid fraction used for the hydroprocessing experiment was derived from the desalted sample by further distilling it using ASTM method D-2592.

2.3 Equipment

A laboratory-scale continuous fixed-bed hydroprocessing unit with a 100-mL tubular reactor was used for all the experiments. A simplified schematic of the unit is provided in Figure 1. The reactor was operated in the upflow mode.

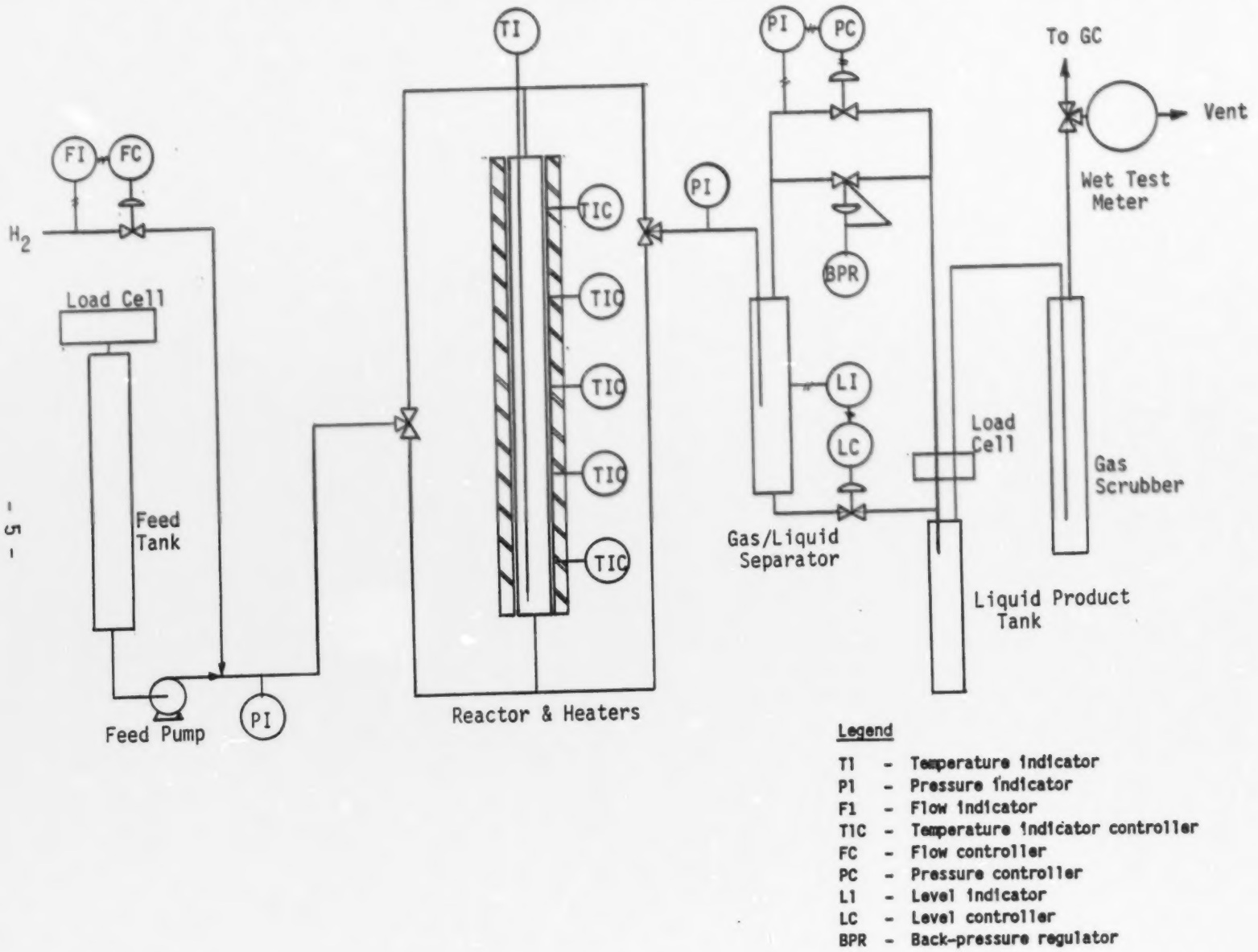

Figure 1. Continuous Hydroprocessing System 100-ml Reactor

The unit has a typical hydroprocessing flow path. The oil feedstock and the hydrogen are mixed before entering the reactor. The unit is configured so that either upflow or downflow operation can be performed. The reactor products are collected in the high-pressure separator where the liquid product is drawn off the bottom and the gas vented out the top. The unit pressure is controlled by a back-pressure regulator (BPR) on the gas outlet. The product gas is scrubbed to remove H_2S then measured in a wet test meter. The liquid product is collected in a weighed tank after draining from the separator.

The oil feed pump, a Zenith gear pump, was capable of pumping very viscous materials reliably. Some leakage problems were encountered, but they could be accommodated and consistent operation still maintained.

A tubular reactor with dimensions of 2.54-cm o.d. x 1.38-cm i.d. x 102-cm long was used for the project. The bed temperature was monitored with an axially-inserted multipoint thermocouple placed in the reactor. The reactor is electrically heated with four individually controlled zones. There are actually five heating elements with two zones (the top two) sharing one controller.

The gas/liquid separator is a simple tube with a level sensing device. A capacitance/inductance probe is used to sense the liquid level in the separator. The probe, which is sensitive to any accumulation of solid particles (coke) on its surface, can change its calibration thus causing erratic operation. Liquid carryover into the gas outlet and loss of the liquid level with gas leaving through the liquid outlet were experienced several times.

The unit pressure was controlled using a back-pressure regulator (BPR). On occasion when the liquid produced was carried over into the gas product system, the PC operation became inconsistent. A second control valve and a controller were installed. More often, consistent pressure control was achieved when the BPR and the control valve operated together. The unit is

capable of handling viscous resid because all liquid lines and some of the gas lines are heat traced.

2.4 Hydroprocessing of Bitumen and Heavy Oil Feedstocks

The experimental program was designed and conducted so that the processing differences among the feedstocks could be identified. Thus feedstocks from the same or identical oil-producing locale were subjected to identical experimental conditions.

2.4.1 Hydroprocessing Conditions

A commercial cobalt-molybdenum (CoMo) high-activity hydroprocessing catalyst, American Cyanamid HDS-20, on alumina support was used for the project. This catalyst has been used on several occassions at the Saskatchewan Research Council and has demonstrated its usefulness as a high-activity catalyst for processing heavier feedstocks.

The fresh catalyst was presulphided prior to use for each feedstock experiment. Presulphiding was performed by loading the 100-mL reactor with between 100-110 g of the fresh catalyst and allowing 10% H_2S in H_2 gas mixture at 400°C and 3.4 MPa to flow through it for approximately four hours.

On completion of the presulphiding, the unit was brought to the following operating conditions:

1. Reactor temperature:
    i) 400°C for the Eyehill feedstocks
    ii) 420°C for Cold Lake and Marguerite Lake feedstocks
2. Reactor pressure: 13.8 mPa
3. LHSV: 0.5 hr^{-1}
4. Hydrogen flow rate: 900 cm^3 H_2/cm^3 of liquid feed
5. Flow mode: upflow

The conditions were maintained for each feedstock test or until a premature termination of the experiment became necessary.

2.4.2 Hydroprocessing of Murphy Eyehill EOR Heavy Oil

The 343°C+ resid fraction was fed to the unit when the desired operating conditions were attained. The feedstock experiment, which had been planned for seven days, lasted just over six days. Periodic plugging of the liquid letdown valve off the gas/liquid separator caused the liquid level in the separator to exceed a present limit thereby causing automatic unit shutdown. Normal operation resumed after the problem was corrected. Shortly after the start of the seventh day of the experiment, however, the reactor plugged and the associated high reactor pressure drop forced the experiment to be terminated.

2.4.3 Hydroprocessing of Undesalted Murphy Eyehill Primary Heavy Oil

The feedstock experiment lasted almost five days. The unit operation was very steady and no automatic shutdowns occurred until a high pressure drop developed across the reactor in a very short period. Attempts to clear the plug failed and the experiment was aborted.

2.4.4 Hydroprocessing of Desalted Murphy Eyehill Primary Heavy Oil

Following presulphiding of the catalyst, the unit was brought to the desired operating conditions and the resid was fed into it. Continuous operation was achieved for about three days until an overnight malfunction of the feedtank heater necessitated the run to be stopped. The problem with the feedtank heater caused the tank temperature to exceed the set point thereby rupturing the pressure line (Tygon tubing) to the tank. This caused considerable loss of the feed material.

The experiment resumed after the heater was replaced. Accumulation of liquid product into the gas product system also caused inconsistent operation of the back-pressure regulator (BPR) and the wet-test meter. The

problem was smoothed out and the run resumed. However, insufficient feed eventually forced the unit to be shutdown. Approximately five of the planned seven days of experiment were completed.

2.4.5 Hydroprocessing of Cold Lake Bitumen

The same processing conditions used for the Eyehill experiments were employed except that the reactor temperature was increased to 420°C. There was reactor line plugging on the first day of the experiment causing unit shutdown. The experiment resumed when the plugged tubings in the reactor upflow and downflow lines were cleared.

Another unit shutdown occurred on day eight of the experiment as a result of a problem with the liquid level control of the separator caused by inadequate flow control by the liquid letdown valve. After the separator probe problem was corrected, normal unit operation resumed until insufficient feed forced termination of the experiment of the eleventh day. A 14-day run had been planned.

2.4.6 Hydroprocessing of Marguerite Lake EOR Bitumen

The processing experiment of the Marguerite Lake resid was slated for seven days, but because of a number of unit operating problems only two days were achieved. The same processing conditions used for the Cold Lake sample were used. A plug developed in the gas/liquid separator inlet line on the first day of the experiment. The liquid level sensor in the separator also provided inconsistent operation. Consequently, the unit was shut down to replace the line and rectify the sensor problems. After about two days of operation, a high pressure drop developed across the reactor catalyst bed. The pressure drop problem persisted despite attempts to clear it. Usual practice is to reverse flow momentarily and then resume normal operation.

The unit was finally shut down to inspect the reactor. A small amount of catalyst was removed from the bottom of the bed (the reactor inlet) and

replaced with fresh catalyst. The reactor was reinstalled and operation resumed. Shortly after the liquid feed was started the reactor plugged again and the unit was shut down. The reactor was removed and the catalyst was found to be plugged with coke. No further work was performed with the Marguerite Lake sample.

2.5 Product Analysis

Liquid products were collected daily, weighed and submitted for simulated distillation, density, carbon, hydrogen, nitrogen and sulphur analyses as specified for each feedstock experiment. Liquid products from selected feed runs were also analyzed for iron, nickel and vanadium. Gas products were sampled approximately two to six times per 24-hour period and analyzed with a gas chromatograph. Average daily analyses for all C_1 through C_6 hydrocarbons plus H_2S, H_2, N_2, CO_2 and CO were determined.

III. RESULTS AND DISCUSSION

3.1 Murphy Eyehill EOR and Primary Heavy Oils

The processing experiment for the 343°C+ resid fraction derived from the Murphy Eyehill EOR heavy crude lasted just over six days. The feedstock analysis, liquid product analysis, yields and calculated conversions are provided in Table 1. The average daily gas analysis is shown in Table 2.

Maintaining steady operation with the EOR feedstock was difficult. The liquid letdown valve of the gas/liquid separator plugged periodically causing the liquid level in the separator to exceed a preset limit. This prompted an automatic unit shutdown. It was felt that the problem was mechanical and totally unrelated to the feedstock's characteristics. Plugging problems are usually caused by a combination of too small of a valve orifice and incorrect line temperature. The shutdowns and subsequent startups caused some inconsistency in the experimental data, but the overall trends were acceptable.

Two forms of the Murphy Eyehill primary feedstock were evaluated; undesalted and desalted. The undesalted feedstock experiment lasted almost five days. The feedstock analysis, liquid product analysis, yields and calculated conversions are provided in Table 3. The average daily gas analysis is presented in Table 4. The unit operation was very steady and no shutdowns were experienced until a high pressure drop developed across the reactor. The experiment was terminated after attempts to clear the plug failed. The plugging problem was attributed to the accumulation of feed salt on the reactor catalyst bed because the reactor plug occurred suddenly, not the usual gradual rise normally experienced with reactor coking.

The desalted feedstock experiment was undertaken to determine if the feed salt was responsible for the processing differences observed with the undesalted sample. The experiment lasted five days. The feedstock analysis, liquid product analysis, yields and calculated conversions are shown in Table

Table 1. Eyehill EOR Resid Liquid Product Analysis and Yields

Sample #	1	2	3	4	5	6	7	Feed
Density (@ 15°C, Kg/m³)	925.4	931.8	907.5	940.1	933.6	949.5	947.7	1020.2
API (@ 15°C)	21.3	20.2	24.3	18.9	19.9	17.4	17.7	7.1
Elemental (wt %)								
Carbon	86.5	86.2	85.9	85.5	85.6	86.4	87	83.7
Hydrogen	11.7	11.7	12.3	11.5	11.6	11.3	11.7	10.1
Nitrogen	0.122	0.152	0.066	0.193	0.168	0.246	0.235	0.344
Sulphur	0.034	0.07	0.021	0.24	0.12	0.31	0.3	3.8
Sim. Dist. (wt %)								
0-210°C	5.4	4.6	5.9	3.9	4.2	3.6	3.7	
210-343°C	17.4	15.4	22.6	13.4	15.9	10.7	11.1	1.4
343-525°C	47.7	47.5	46.4	44.8	48	42.8	42.6	32.8
525°C	29.5	32.5	25.1	37.9	31.9	42.9	42.6	65.8
Trace Metals (wppm)								
Fe	128	84.2	55.5	87.9	59.8	88	15.6	611
Ni	7	8.9	4.3	12.5	7.6	15.3	16.5	68.2
V	15.1	17.2	10.5	21.2	18.8	33.6	44.5	189
Tol. Insol. (wt %)	0.67	0.37	0.16	0.73	0.58	0.53	0.56	0.74
nC_6 Insol. (wt %)	3.3	3.8	1.34	5.4	4.2	6.5	5.9	17.2
RCR (wt %)	3.5	4.4	1.9	5.9	4.7	7.2	7	
Conversion (wt %)								
Sulphur	99.15	98.30	99.49	94.13	97.27	91.85	92.77	
Nitrogen	66.34	59.30	82.17	47.87	57.79	28.53	37.43	
525°C	57.45	54.50	64.56	46.49	58.09	34.84	40.70	
Sulphur (H_2S)	85.09	78.74	76.72	87.31	112.95	34.72	39.28	
Yield (wt.% liq. feed)								
Liquid	94.9	92.1	92.9	92.9	86.4	99.9	91.6	
Gas	13.8	12.4	14.1	15.0	24.3	8.3	9.4	
H_2 Consumption (g mol H_2/g liq. feed)	0.0108	0.0102	0.0072	0.0097	0.0145	0.0115	0.0057	

Table 2. Average Daily Gas Analysis--Eyehill EOR Resid

Day	1	2	3	4	5	6
Component (mol %)						
C_5+	0.729	0.598	0.451	0.512	0.366	0.361
Hydrogen	93.131	93.540	94.773	94.534	95.845	96.138
C_3H_8	0.427	0.389	0.335	0.330	0.266	0.277
C_3H_6						
H_2S	3.358	3.308	2.521	2.774	1.939	1.709
$i\text{-}C_4H_{10}$	0.129	0.121	0.101	0.109	0.083	0.078
$n\text{-}C_4H_{10}$	0.277	0.234	0.201	0.200	0.157	0.173
$1\text{-}C_4H_8$						
$i\text{-}C_4H_8$						
$n\text{-}C_4H_8$						
$t\text{-}2\text{-}C_4H_8$						
$i\text{-}C_5$	0.091	0.078	0.068	0.072	0.059	0.059
$n\text{-}C_5$	0.136	0.114	0.097	0.103	0.077	0.080
C_2H_4						
C_2H_6	0.501	0.456	0.391	0.387	0.305	0.299
N_2	0.098	0.111	0.153	0.091	0.195	0.142
CH_4	1.126	1.051	0.909	0.888	0.708	0.683
CO						
TOTAL	100.003	100.000	100.000	100.000	100.000	99.999

Table 3. Undesalted Eyehill Primary Liquid Product Analyses and Yields

Sample #	1	2	3	4	5	Feed
Density (@ 15°C, Kg/m³)	938.5	948.6	956.2	958.8	959.4	1024.1
API (@ 15°C)	19.1	17.5	16.3	15.9	15.8	6.5
Elemental (wt %)						
Carbon					85.8	84.2
Hydrogen					11.6	10.2
Nitrogen	0.172	0.227	0.253	0.263	0.282	0.3826
Sulphur	0.27	0.49	0.72	0.83	0.92	3.79
Sim. Dist. (wt %)						
0-204°C	3.4	2.7	2.5	2.6	2.3	0
204-343°C	10.6	9.1	8.4	8.3	8	0
343-525°C	44.2	42.3	42.9	43.9	42.1	36.7
525°C	41.8	45.9	46.2	45.2	47.6	63.3
Trace Metals (wppm)						
Fe					14.8	48.2
Ni					24	61.9
V					14.6	260
Tol. Insol. (wt %)					0.71	1.52
nC_5 insol. (wt %)						
RCR insol. (wt %)						
Conversion (wt %)						
Sulphur	93.40	87.88	81.53	82.89	76.78	
Nitrogen	58.33	44.37	35.71	38.07	29.49	
525°C	38.79	32.01	29.04	35.67	28.07	
Sulphur (H_2S)	53.65	60.79	43.12	65.06	63.93	
Yield (wt % liq. feed)						
Liquid	92.7	93.8	97.2	90.1	95.7	
Gas	9.7	10.2	9.4	9.8	10.2	
H_2 Consumption	0.0079	0.0066	0.0054	0.0048	0.0068	
(gmol H_2/g liq. feed)						

Table 4. Average Daily Gas Analysis--Undesalted Eyehill Resid

Day	1	2	3	4	5
Component (vol %)					
C_6+	0.497	0.490	0.333	0.364	0.246
Hydrogen	95.122	95.037	96.494	95.326	95.362
C_3H_8	0.278	0.246	0.158	0.218	0.174
C_3H_6					
H_2S	2.510	2.697	1.786	2.897	2.659
i-C_4H_{10}	0.088	0.081	0.062	0.075	0.069
n-C_4H_{10}	0.175	0.147	0.112	0.130	0.113
1-C_4H_8					
i-C_4H_8					
n-C_4H_8					
t-2-C_4H_8					
i-C_5	0.060	0.050	0.037	0.045	0.037
n-C_5	0.087	0.074	0.054	0.066	0.053
C_2H_4					
C_2H_6	0.330	0.293	0.254	0.255	0.244
N_2	0.095	0.199	0.082	0.030	0.458
CH_4	0.758	0.687	0.628	0.593	0.586
CO					
TOTAL	100.000	100.001	100.000	99.999	100.001

5. The average daily gas analysis is provided in Table 6. No plugging problem was encountered during the experiment. The problem with the feedtank heater, which caused considerable loss of the feedstock, was partially responsible for the premature termination of the experiment.

The tabulated data for the Murphy Eyehill feedstock experiments are presented graphically in Figures 2 through 5. Figure 2 compares the sulphur and nitrogen conversion of the EOR and the undesalted (U-Prim) and desalted (D-Prim) primary feedstocks.

Sulphur conversion for the EOR resid averaged about 96 wt % and was significantly greater throughout the experiment than was the case with the primary feedstocks. The sulphur conversion levels for the two forms of the primary feedstock were comparable up to day two of each experiment, but afterwards the superior performance of the desalted sample was evident. As expected, sulphur conversion was high on the first day of the experiment for all samples demonstrating the effect of initial high catalyst activity. This high catalyst activity was maintained for the EOR feedstock up to the third day of unit operation when the catalyst's desulphurization activity started to decline.

The catalyst appeared to be deactivating faster for the undesalted resid as indicated by the steeper sulphur conversion curve. Beyond the first day of the desalted sample experiment, the sulphur conversion was virtually constant at an average of 89 wt %, indicating the catalyst's ability to maintain its desulphurization activity for an extended period improved by desalting the sample. Similar trends can be seen in the nitrogen conversion characteristics of the three samples, also shown in Figure 2.

Figure 3 compares the resid conversion of the three feedstocks. Again the highest conversion of the 525°C+ material was achieved with the EOR feedstock. The conversion was consistently about 20 percentage points greater than for the primary resid. There was little difference in the conversion for the two primary samples indicating that desalting had no discernable

Table 5. Desalted Eyehill Primary Resid Liquid Product Analyses and Yields

Sample #	1	2	3	4	5	Feed
Density (@ 15°C, Kg/m³)	938.60	944.40	948.20	949.90	947.30	1014.50
API	19.10	18.20	17.60	17.30	17.70	7.90
Elemental (wt %)						
Carbon	85.70				86.40	85.30
Hydrogen	11.70				11.60	10.40
Nitrogen	0.22	0.24	0.25	0.24	0.24	0.39
Sulphur	0.33	0.44	0.39	0.40	0.43	3.67
Sim. Dist. (wt %)						
0-204°C	3.50	2.80	2.70	2.60	0.00	0.0
204-343°C	9.80	9.10	10.70	10.00	0.00	0.00
343-525°C	48.00	47.50	47.80	47.70	49.30	33.40
525°C+	38.70	40.60	38.80	39.20	38.00	~~52.40~~ 66.60
Trace Metals (wppm)						
Fe						49.80
Ni						57.80
V						100.00
Tol. Insol. (wt %)						0.03
nC_5 Insol. (wt %)						
RCR (wt %)						
Conversion (wt %)						
Sulphur	91.84	87.76	90.00	89.24	89.02	
Nitrogen	51.65	41.93	41.00	39.60	42.43	
525°C+	32.94	27.38	30.35	26.34	32.06	
Yield (wt % liq. feed)						
Liquid	90.80	93.70	94.10	98.70	93.70	
Gas	4.70	6.20	5.00	5.30	4.60	
H_2 Consumption (gmol H_2/g liq. feed)	0.0077	0.0087	0.0094	0.0047	0.0091	

Table 6. Average Daily Gas Analysis--Desalted Eyehill Primary Resid

Day	1	2	3	4	5
Component (vol %)					
C_6+	0.434	0.298	0.357	0.215	0.310
Hydrogen	94.441	94.762	95.083	96.891	95.660
C_3H_8	0.269	0.203	0.256	0.174	0.193
C_3H_6					
H_2S	3.202	3.503	2.945	1.828	2.709
i-C_4H_{10}	0.071	0.049	0.061	0.020	0.041
n-C_4H_{10}	0.139	0.124	0.143	0.107	0.119
1-C_4H_8					
i-C_4H_8					
n-C_4H_8					
t-2-C_4H_8					
i-C_5	0.049	0.040	0.046	0.031	0.039
n-C_5	0.073	0.061	0.071	0.047	0.058
C_2H_4					
C_2H_6	0.336	0.277	0.316	0.202	0.258
N_2	0.226	0.060	0.037	0.051	0.041
CH_4	0.760	0.624	0.687	0.433	0.519
CO	0.000	0.000	0.000	0.000	0.052
TOTAL	100.000	100.000	100.000	100.000	100.000

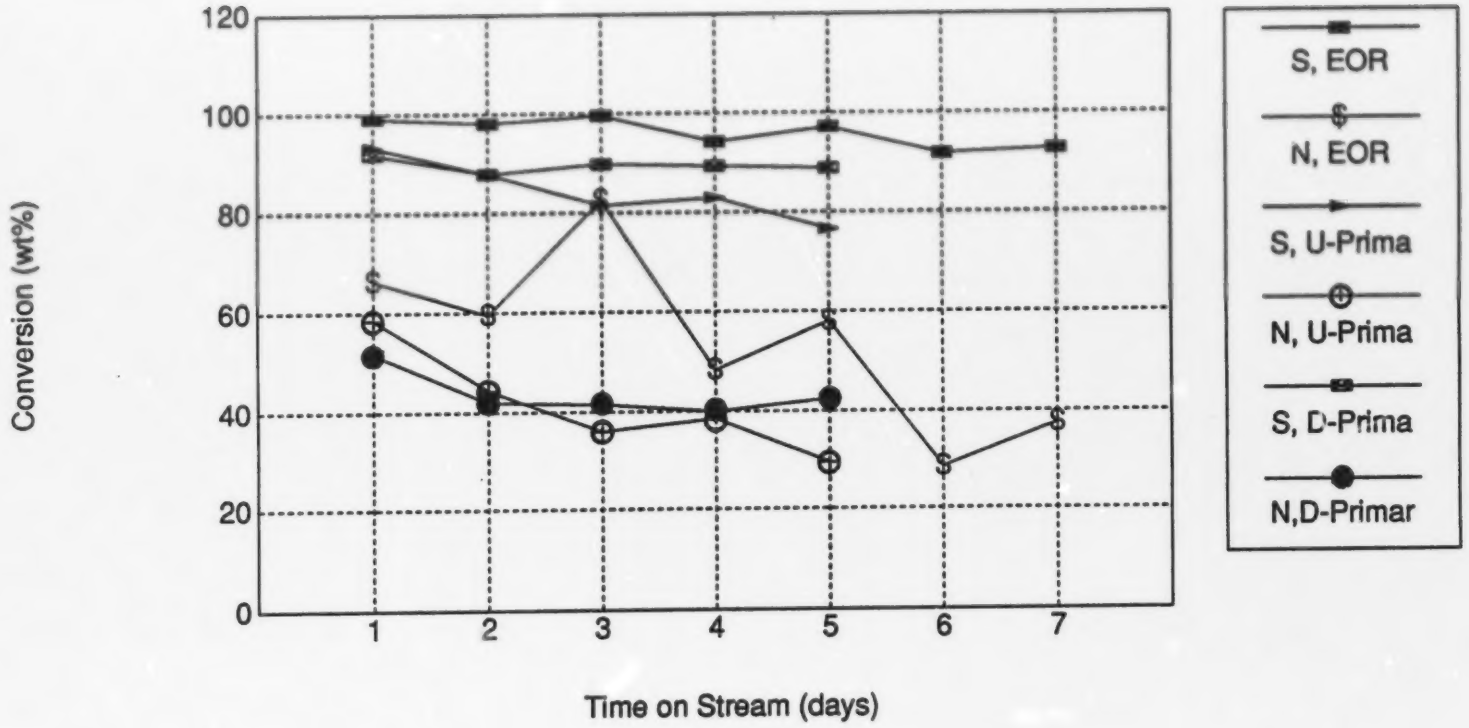

Figure 2: Sulphur, Nitrogen Conversion

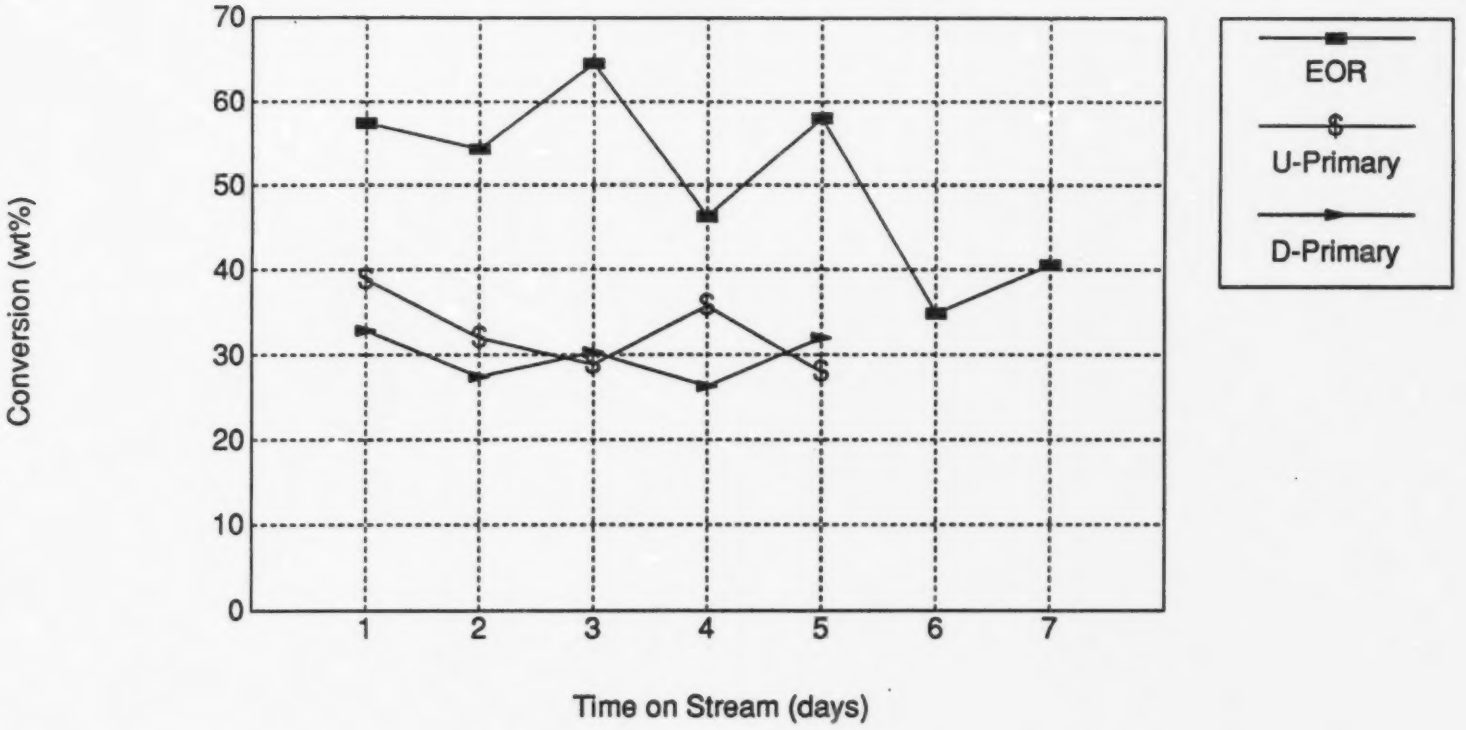

Figure 3: Resid (525 C+) Conversion

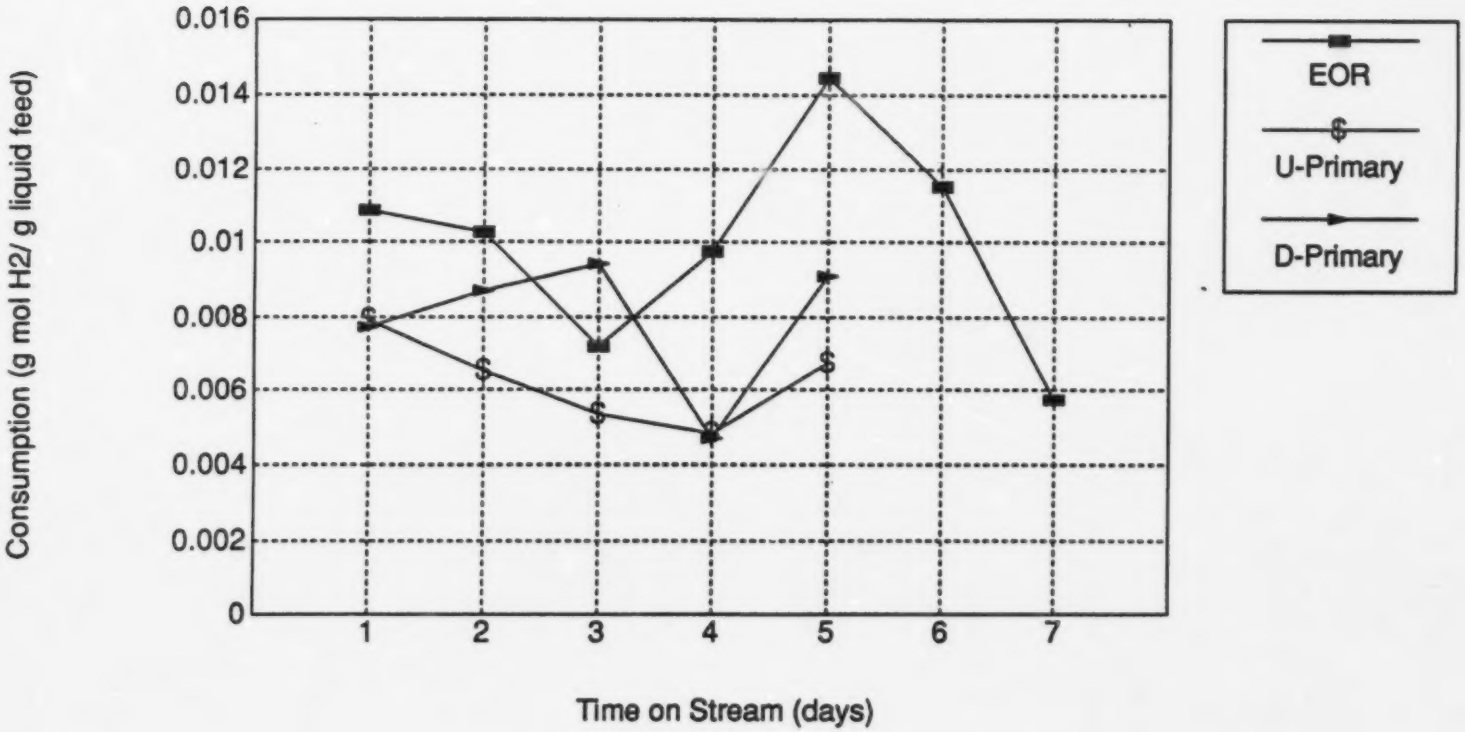

Figure 4: Hydrogen Consumption

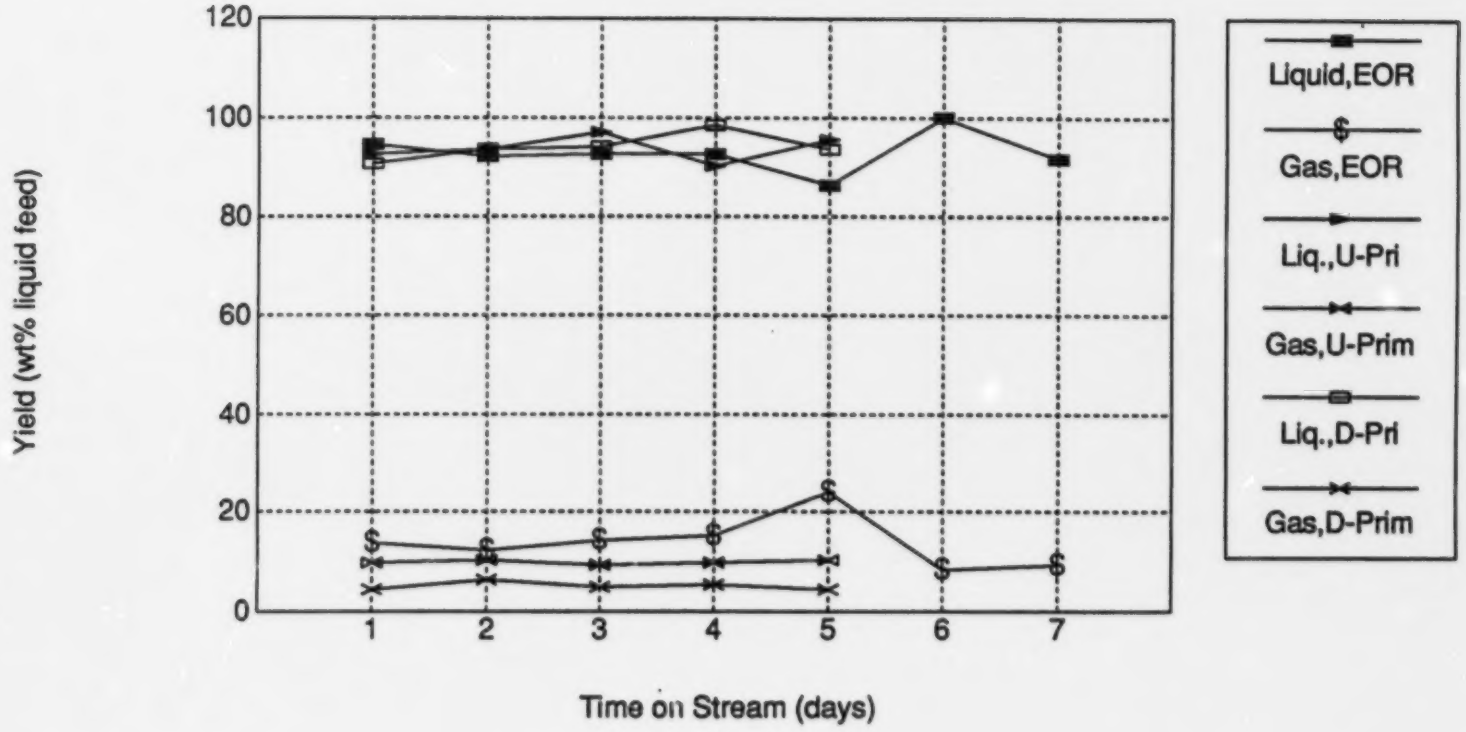

Figure 5: Product Yields

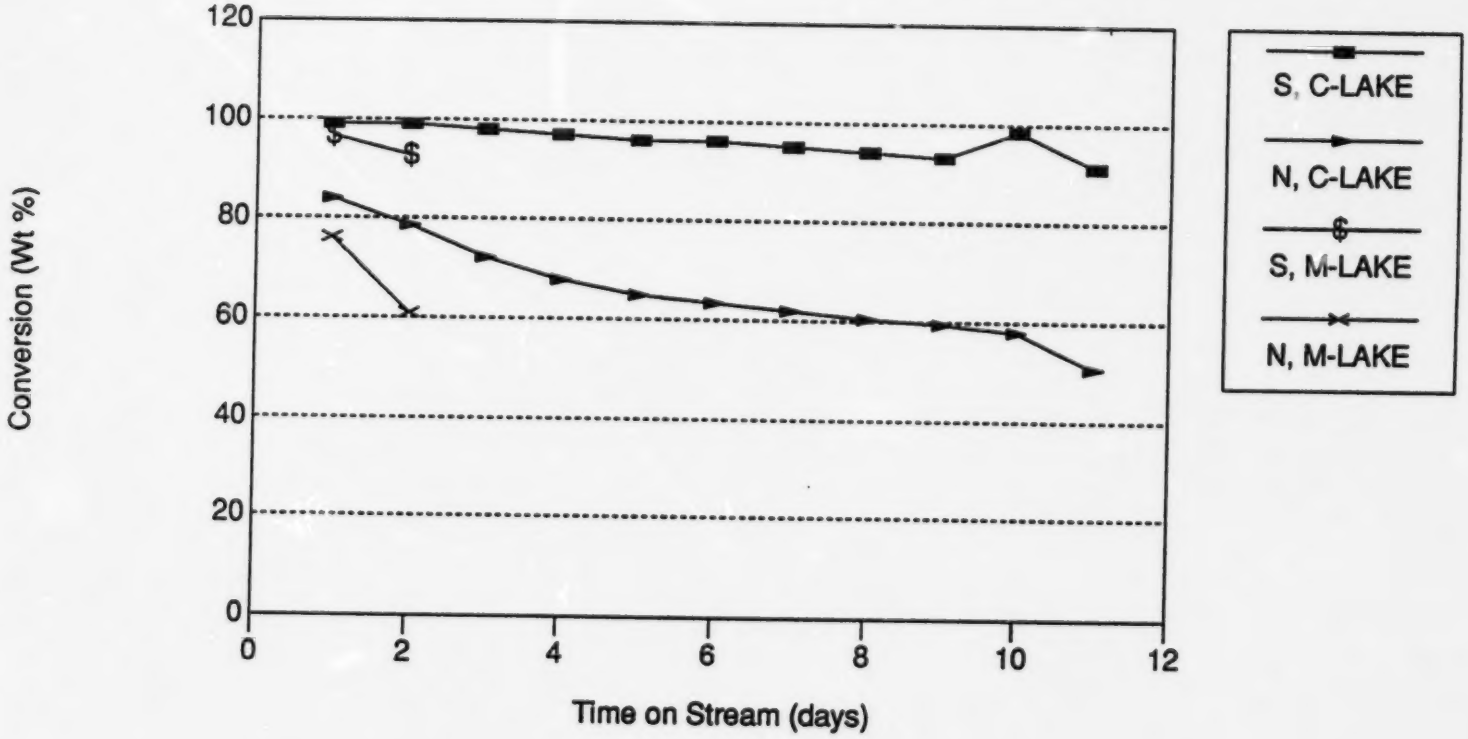

Figure 6: Sulphur, Nitrogen Conversion

effect on the conversion of the 525°C+ material. Resid conversion is largely a result of thermal conditions not catalyst activity, which means the EOR sample contained easier to convert components.

The hydrogen consumption data are shown in Figure 4. The EOR sample had consistenly greater hydrogen consumption relative to the primary feedstocks particularly beyond the fourth day of the experiment. This is due in part to the higher sulphur and nitrogen conversons achieved. A significant amount of the hydrogen is used in the conversion of sulphur to H_2S and nitrogen to NH_3. The hydrogen consumption of the desalted feedstock relative to the undesalted was greater until the fourth day when a reduction in catalyst activity caused both to experience a lower consumption level.

The liquid and gas yields are compared in Figure 5. No significant difference can be observed among the yields of the three feedstocks. The gas yield for the EOR feed was slightly greater than for the primary samples. This is due in part to the greater H_2S production.

The particularly superior performance of the EOR feedstock over the primary samples was identified in this study. The sulphur, nitrogen and resid (525°C+) material conversions were consistently higher than those for the primary feedstocks. The opposite observation was expected for the EOR sample because it is generally agreed that the thermal recovery method can alter the characteristics of the feedstock thereby rendering it difficult to process. Because the three samples had similar physical/chemical properties, with the exception of the iron content which was higher (611 wppm) for the EOR sample relative to about 50 wppm for the primary variety, it is possible the iron level of the EOR material aided the catalyst performance by suppressing coke formation.

3.2 Cold Lake and Marguerite Lake Bitumen Feedstocks

The Cold Lake feedstock experiment lasted approximately eleven days. It was planned for fourteen days. The feedstock analysis, liquid product analysis, yields and calculated conversions are provided in Table 7. The

Table 7. Cold Lake Resid Liquid Product Analysis and Yields

Sample #	1	2	3	4	5	6	7	8	9	10	11	Feed
Density (@ 15°C, Kg/m³)	896.50	900.00	904.70	907.80	910.70	912.10	913.20	914.80	916.30	917.20	918.70	1011.20
API (@ 15°C)	26.10	25.60	24.80	24.20	23.70	23.50	23.30	23.00	22.80	22.60	22.40	8.30
Elemental (wt %)												
Carbon	85.80									86.20		83.50
Hydrogen	12.60									12.00		10.50
Nitrogen	0.07	0.09	0.12	0.14	0.15	0.16	0.17	0.17	0.18	0.19	0.19	0.39
Sulphur	0.06	0.04	0.10	0.16	0.21	0.22	0.26	0.33	0.37	0.40	0.45	5.04
Sim. Dist. (wt %)												
IBP-204°C	8.40	7.60	7.40	6.90	6.70	6.60	6.40	6.30	6.10	5.90	5.90	0.00
204-343°C	27.50	27.20	25.40	25.20	23.90	23.50	23.30	22.80	22.50	22.10	21.70	5.60
343-525°C	49.20	49.90	46.90	46.30	46.80	46.60	45.80	45.20	44.60	45.50	43.90	33.20
525°C+	14.90	15.30	20.30	21.60	22.60	23.30	24.50	25.70	26.80	26.50	28.50	61.20
Trace Metals (wppm)												
Fe	12.30									5.00		25.40
Ni	2.80									7.60		73.90
V	4.00									7.40		255.00
Tol. Insol. (wt %)	0.07									0.07		0.04
nC_5 Insol. (wt %)	0.79									3.10		
RCR (wt %)												
Conversion (wt %)												
Sulphur	98.83	99.29	98.18	97.13	96.22	96.04	95.36	94.09	93.32	98.76	91.01	
Nitrogen	84.04	78.41	72.00	67.87	64.74	63.43	61.88	60.12	59.14	57.73	50.65	
525°C+	78.13	77.37	69.51	68.08	66.47	65.50	64.00	62.08	60.17	61.23	53.09	
Yield (wt.% liq. feed)												
Liquid	89.80	90.50	91.90	90.40	90.80	90.60	89.90	90.30	91.00	89.50	100.70	
Gas	11.80	10.30	11.50	11.30	10.80	8.80	9.20	13.60	10.10	9.70	17.20	
H_2 Consumption (g mol H_2/g liq. feed)	0.0135	0.0112	0.0099	0.0084	0.007	0.0074	0.0070	0.0048	0.0063	0.0055	0.0054	

average daily gas analysis is presented in Table 8. Reactor inlet line plugging and the associated inconsistent operation of the separator liquid level probe were the two main problems encountered during the experiment.

The reactor upflow line plugging was corrected by replacing the affected lines. The trim set on the valve was increased to minimize plugging.

The Marguerite Lake EOR resid experiment lasted only two days. Table 9 shows the feedstock, liquid product, yields and calculated conversion analyses. The average daily gas analysis is shown in Table 10. Plugging in the gas/liquid separator inlet line on the first day of the experiment necessitated a temporary unit shutdown. A more serious problem was the plugging of the catalyst and the associated high pressure drop across the catalyst bed. The catalyst plugging appeared to be coke formation, because of a steady increase in reactor pressure over the two days. Salt in the feed may have been a problem, but it was not analyzed because Cold Lake feeds are usually low in salt.

The tabulated data for Cold Lake and Marguerite Lake resids are presented graphically in Figures 6 through 9. Figure 6 compares the sulphur and nitrogen conversion levels.

Sulphur conversion for the Cold Lake sample was approximately constant at 96 wt % on the average for the duration of the experiment. The catalyst deactivation, as reflected by the gradual reduction in sulphur conversion, was also moderate.

Nitrogen removal was also high early in the run, but gradually declined as the catalyst denitrogenation activity declined as the experiment progressed. By the eleventh day, the nitrogen conversion had fallen to about 51 wt % from a value of approximately 80 wt % on day one.

The short duration of the Marguerite Lake EOR resid experiment generated insufficient data for a more comprehensive graphical representation. The

Table 8. Average Daily Gas Analysis--Cold Lake Resid

Day	1	2	3	4	5	6	7	8	9	10	11
Component (vol %)											
C_6+	0.980	0.735	0.701	0.870	0.797	0.568	0.636	0.609	0.746	0.704	0.851
Hydrogen	87.432	89.414	89.610	90.072	90.568	92.109	92.005	92.307	91.586	91.990	91.167
C_2H_6	0.722	0.551	0.603	0.555	0.453	0.436	0.462	0.455	0.491	0.464	0.520
C_3H_6	0.082	0.058	0.000	0.000	0.085	0.000	0.000	0.000	0.000	0.000	0.000
H_2S	6.691	6.197	5.862	5.643	5.619	4.621	4.538	4.290	4.764	4.521	4.972
$1\text{-}C_4H_{10}$	0.739	0.514	0.565	0.466	0.299	0.163	0.202	0.177	0.182	0.174	0.193
$n\text{-}C_4H_{10}$	0.598	0.261	0.388	0.359	0.148	0.214	0.244	0.235	0.271	0.243	0.303
$1\text{-}C_4H_8$											
$1\text{-}C_4H_8$											
$t\text{-}C_4H_8$											
$c\text{-}C_4H_8$											
$1\text{-}C_5H_{12}$	0.187	0.126	0.125	0.121	0.108	0.080	0.088	0.085	0.099	0.088	0.113
$n\text{-}C_5H_{12}$	0.263	0.175	0.168	0.166	0.151	0.107	0.123	0.118	0.134	0.121	0.160
C_2H_4											
C_3H_6	0.782	0.626	0.634	0.495	0.552	0.518	0.521	0.523	0.543	0.523	0.547
N_2	0.000	0.006	0.000	0.007	0.021	0.036	0.006	0.016	0.004	0.004	0.016
CH_4	1.522	1.336	1.343	1.246	1.199	1.147	1.175	1.184	1.180	1.168	1.158
CO											
TOTAL	99.998	99.999	99.999	100.000	100.000	99.999	100.000	99.999	100.000	100.000	100.000

Table 9. Marguerite Lake EOR Resid Liquid Product Analyses and Yields

Day	1	2	Feed
Density (@ 15°C, Kg/m³)	905.40	910.10	1023.90
API (@ 15°C)	24.60	23.80	6.60
Elemental (wt %)			
Carbon	85.70		83.60
Hydrogen	12.20		10.20
Nitrogen	0.15	0.23	0.52
Sulphur	0.21	0.43	5.42
Sim Dist (wt %)			
IBP-204°C	9.00	9.90	
204-343°C	21.00	20.50	
343-525°C	48.90	46.70	29.50
525°C+	21.10	22.90	70.50
Trace Metals (wppm)			
Fe			28.10
Ni			269.00
V			274.00
Tol. Insol (wt %)			3.78
nC_5 Insol (wt %)			
RCR (wt %)			
Conversion (wt %)			
Sulphur	96.58	92.82	
Nitrogen	74.85	60.77	
525°C+	73.60	43.76	
Yield (wt % liq feed)			
Liquid	88.20	90.50	
Gas	9.80	6.00	
H_2 Consumption (gmol H_2/g liq feed)	0.0149	0.257	

Table 10. Average Daily Gas Analysis--Marguerite EOR Resid

Day	1	2
Component (vol %)		
C_6+	0.579	0.659
Hydrogen	88.711	86.621
C_3H_8	0.827	0.943
C_3H_6		
H_2S	6.043	5.717
$i\text{-}C_4H_{10}$	0.255	0.260
$n\text{-}C_4H_{10}$	0.477	0.458
$1\text{-}C_4H_8$		
$i\text{-}C_4H_8$		
$n\text{-}C_4H_8$		
$t\text{-}2\text{-}C_4H_8$		
$i\text{-}C_5$	0.149	0.159
$n\text{-}C_5$	0.203	0.219
C_2H_4		
C_2H_6	0.877	1.232
N_2	0.149	0.431
CH_4	1.731	3.300
CO		
TOTAL	100.001	99.999

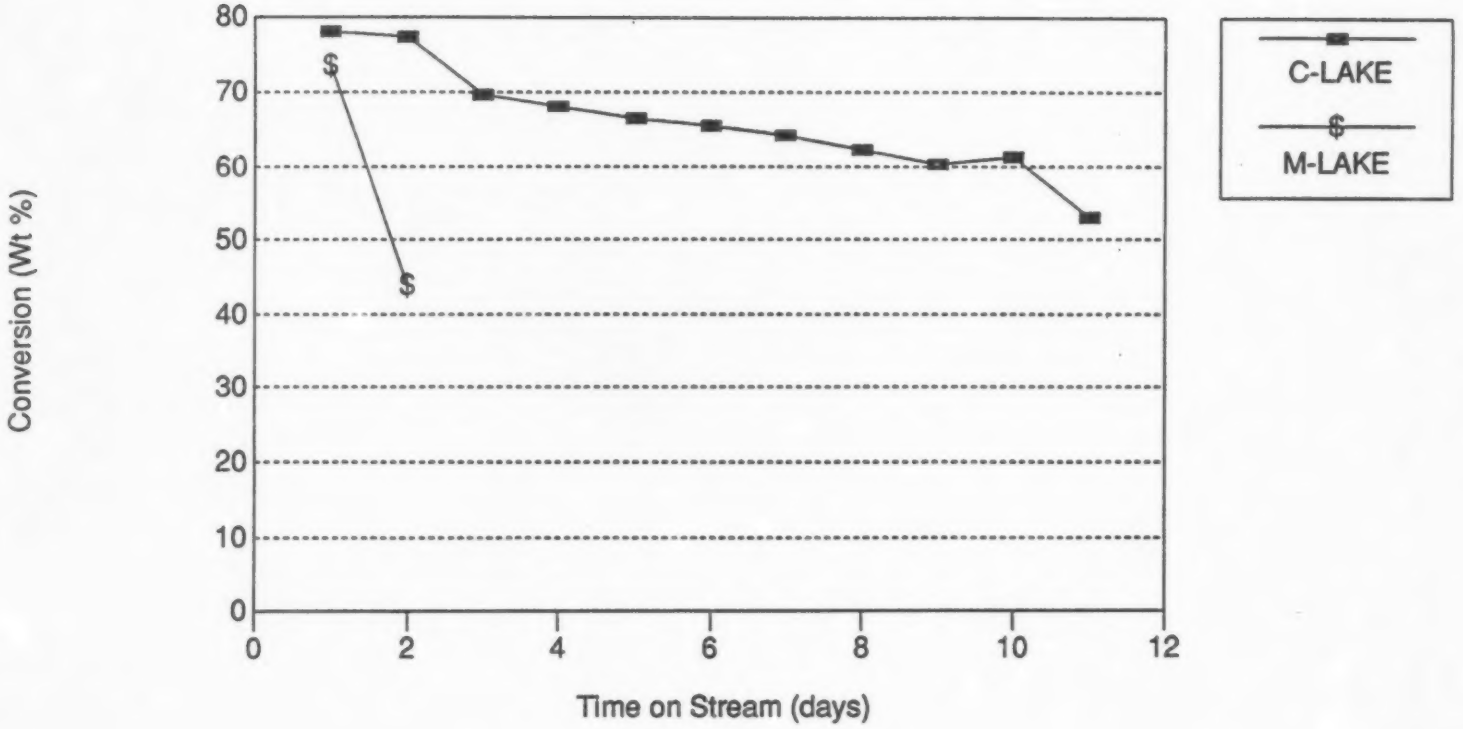

Figure 7: Resid (525 C+) Conversion

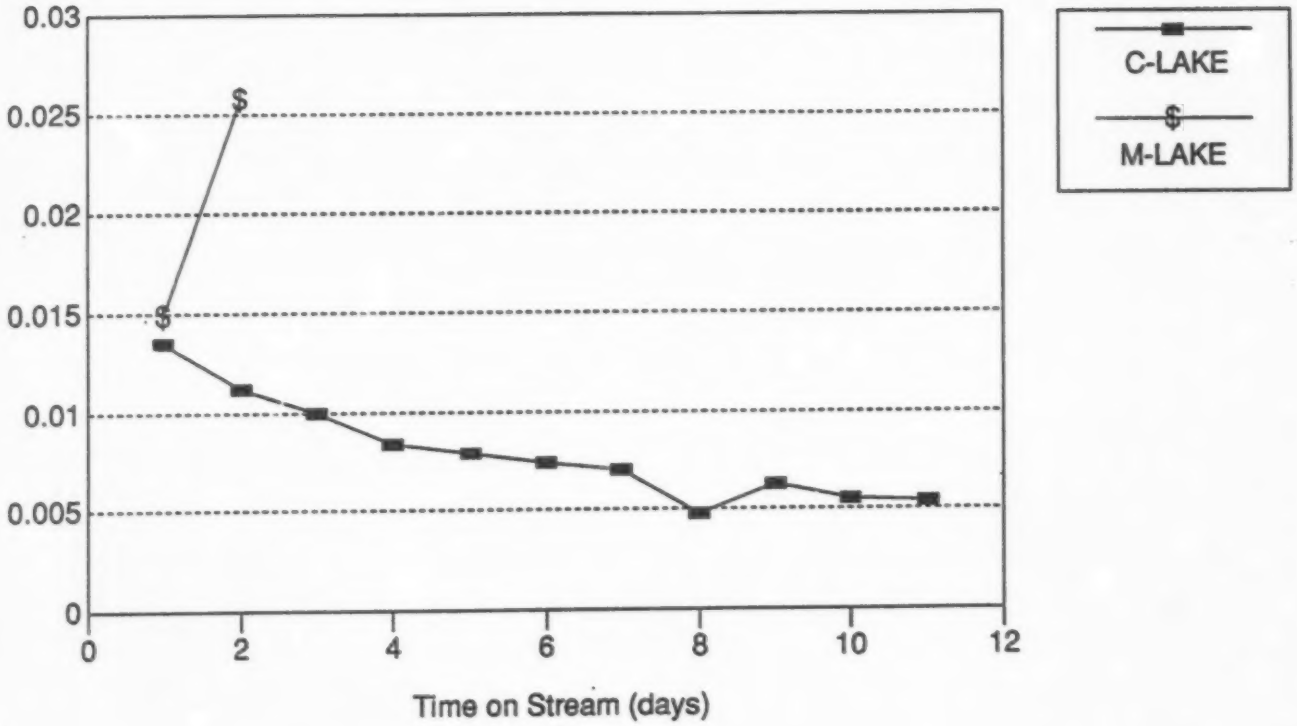

Figure 8: Hydrogen Consumption

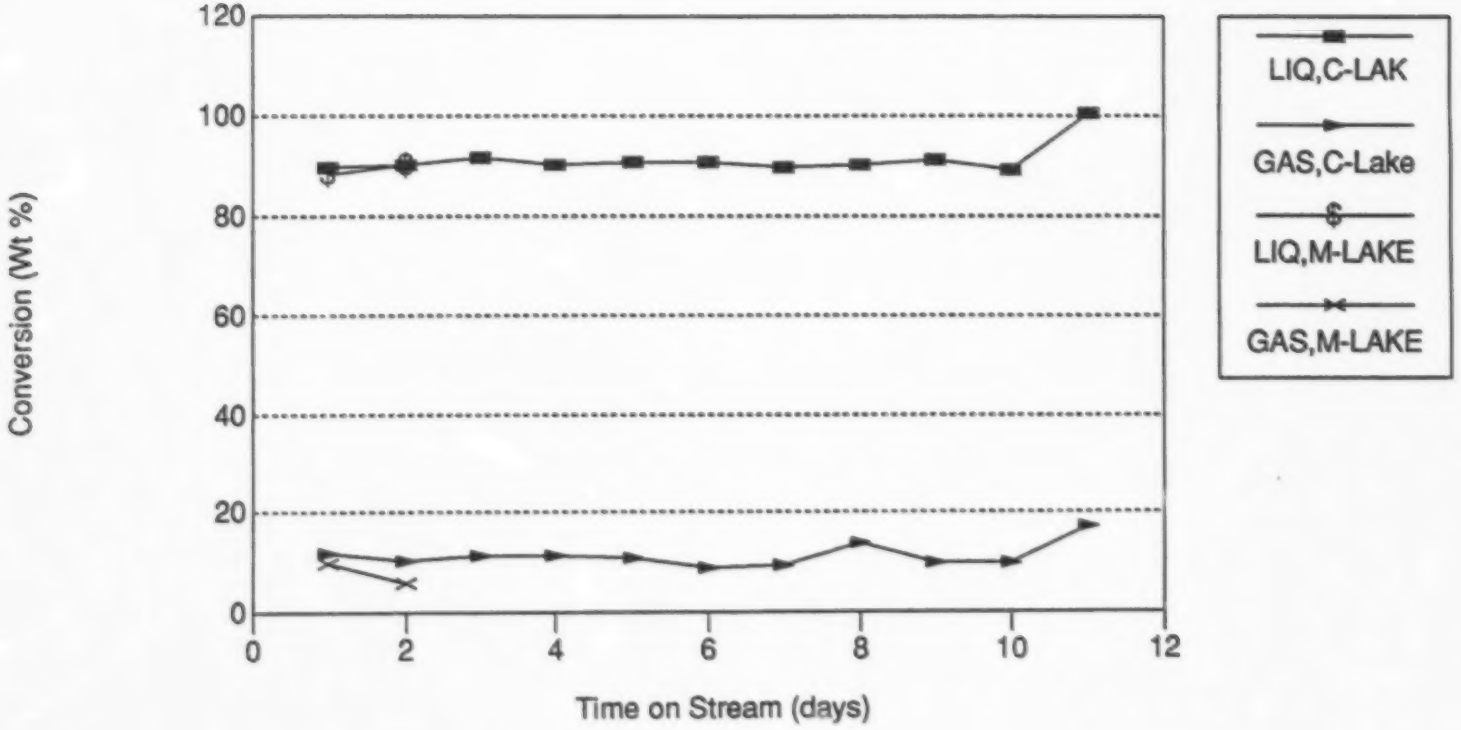

Figure 9: Product Yields

general trend of the sulphur removal plot, however, indicates a faster catalyst deactivation and a corresponding lower sulphur conversion relative to the Cold Lake feed.

The nitrogen conversion plots are steeper indicating a more significant daily loss in catalyst activity for nitrogen conversion as the experiments progressed.

The resid conversion depicted in Figure 7 shows that the conversion of the 525°C+ material of the Cold Lake sample was fairly high and constant at about 78 wt % up to the second day of the experiment. Thereafter, there was a daily step-wide reduction in conversion as the catalyst activity dropped. This averaged about 64 wt % until the end of the experiment.

Generally, the performance of the Marguerite Lake EOR feedstock was poorer in comparison to the Cold Lake sample. By the end of the second day of unit operation, the conversion had already dropped by approximately 30 percentage points reflecting a faster catalyst deactivation.

The hydrogen consumption data are compared in Figure 8. The hydrogen consumption data of the Cold Lake feedstock exhibit the same general trend of a reduction in consumption as the catalyst activity dropped, particularly for sulphur and nitrogen conversion. More hydrogen is required to convert sulphur to H_2S and nitrogen to NH_3 and vice versa. The hydrogen consumption plot of the Marguerite Lake sample shows an opposite trend that can largely be attributed to the observed general poor processing characteristics of the feedstock.

The liquid and gas yields are compared in Figure 9. The Cold Lake sample had fairly constant daily liquid and gas yields that averaged 91 and 11 wt %, respectively, for the duration of the experiment. The sudden increase of the liquid product near the end of the run can be attributed to

equipment problems. The separator was drained completely because sensor problems resulted in the collection of additional liquid product. A similar trend can be observed in the liquid and gas yields of the Marguerite Lake EOR feedstock.

IV. CONCLUSIONS AND RECOMMENDATIONS

The resid (343°C+) derived from the Murphy Eyehill heavy crude produced by the fireflood EOR method was clearly easier to hydroprocess when compared to the resid from the primary production crude. At comparable operating conditions, the EOR sample achieved greater sulphur, nitrogen and resid (525°C+ material) conversions. Batch reaction experiments performed at the Saskatchewan Research Council (SRC) have previously indicated that fireflood EOR resids are more difficult to process. The contribution of the iron in the EOR sample in improving its processability must be acknowledged.

At similar operating conditions, the Cold Lake bitumen sample produced higher sulphur, nitrogen and resid conversions as well as greater liquid and gas yields, and appeared to have had a better hydroprocessing performance than the Marguerite fireflood EOR bitumen feedstock. Extended period experimentation with the Marguerite Lake feedstock may be necessary, however, to properly compare the performance of the two feedstocks.

A good cleaning and desalting procedure is essential to properly evaluate the true response of a feedstock to hydroprocessing. Cleaning and desalting the primary resid feedstock markedly improved its processing characteristics. Reactor plugging, which plagued the undesalted primary resid experiment, was absent. Catalyst deactivation was considerably less and the catalyst ability to maintain a constant desulphurization activity for an extended period was greatly improved.

It is recognized that if the samples used in this project had been cleaned and desalted prior to distillation, a very different result may have been achieved. The iron levels of the Eyehill EOR sample as well as the salt contents of the other feedstock would have been significantly reduced by the cleaning and desalting processes.

Further process studies should be performed with clean, desalted counterparts of the undesalted feedstock used in this project to properly assess their true hydroprocessing characteristics.